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AUTHORITY

USAF ltr, 2 Mar 1972

REVIEW OF RECENT DEVELOPMENTS

Oxidation-Resistant Coatings for Refractory Metals

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July 15, 1966

EVALUATION OF COATINGS IN AEROSPACE ENVIRONMENTS

A comprehensive study of the behavior of protective coatings in simulated aerospace environments has been conducted at Lockheed.(1) Eight commercial or advanced pilot-scale coatings were examined: Pfaudler PFR-6, Chromizing Durak B, and Boeing Disil coatings on molybdenum alloy TZM; Pfaudler PFR-32, Vought IV, and TRW Cr-Ti-Si coatings on columbium alloy Cb-752; the TRW Cr-Ti-Si coating on columbium alloy B-66, and the GT&E Sn-Al coating on Ta-10W. These coating systems were evaluated as follows:

(1) The maximum temperatures (2400 to 3300 F) for coating lifetimes of 30, 60, 120, and 240 minutes in air at pressures of 0.01, 0.1, 1.0, 5, 20, and 50 torr were determined (baseline data).

(2) Tests were conducted in air flowing over the surface at mach 3 velocity.

(3) Structural changes caused by heating the coatings in high vacuum were investigated.

(4) Temperature and pressure cycling studies were performed to determine the effects of various environments and multimission use on performance capabilities.

(5) The ability to predict performance of heat-shield components was evaluated by conducting step-oxidation tests (termed "kinetic model tests") according to calculated re-entry profiles.

(6) Defect tolerance studies were conducted, which included an assessment of the coatings' resistance to defect formation caused by mechanical strain, impact, and vibration.

(7) The ability to repair defective coatings was examined.

(8) Compatibility studies were performed between the different coating systems and and also with various insulation materials.

The report also contains an informative discussion of the requirements of coated refractory metals in various aerospace applications.

A short summary of Lockheed's findings is given below.

Effect of Reduced Air Pressure. Figure 1 represents a comparison of the 4-hr random failure limits, baseline results, for the seven coating systems.

Coating performance in the 1 to 50 torr range was controlled by random defects for the silicide-base systems. Fine hairline fissures in these coatings became sites for local failures. The Cr-Ti-Si coatings on the columbium alloys exhibited somewhat different behavior than the other silicide coatings. The Cr-Ti-Si coatings were more tolerant to fissures, and performance was limited by coating composition variations, which caused localized melting at temperatures above 2600 F. Performance of the Sn-Al coating on tantalum in the 1 to 50 torr range was relatively insensitive to pressure variations at temperatures below 3000 F, where rapid boiling of the liquid tin did not occur. Diffusion between the coating and the substrate did occur at rapid rates at temperatures above 2800 F in the Sn-Al system.

In the 0.01 to 1.0 torr range, all silicide coatings on the molybdenum and columbium alloys had essentially the same performance capabilities. The systems had a useful coating life of 4 hours at temperatures of 2550 to 2650 F, but exhibited random failure in less than 1 hour above 2650 F. The Sn-Al coating on Ta-10W showed a marked decrease in performance at temperatures above 2200 F in this low-pressure range.

The authors also noted that internal surfaces of re-entry vehicles can be exposed to pressures below 1 torr during periods of peak heating. Structures could conceivably fail from the inside out.

Gas-Velocity Effects. Mach 3 air flow affected the performance of the coatings only when liquid or viscous conditions existed on the surface. For all coating systems with TZM as the substrate, no effect of flow was noted at temperatures below 2900 F and pressures of 5 to 20 torr. The behavior of the silicide coatings on columbium was generally the same.

Vacuum Volatility Effects. Silicide-base coatings on the molybdenum and columbium alloys can withstand preheating in vacuum for 30 to 60 minutes at 2600 to 2800 F with little change in baseline coating behavior. The Sn-Al coating on

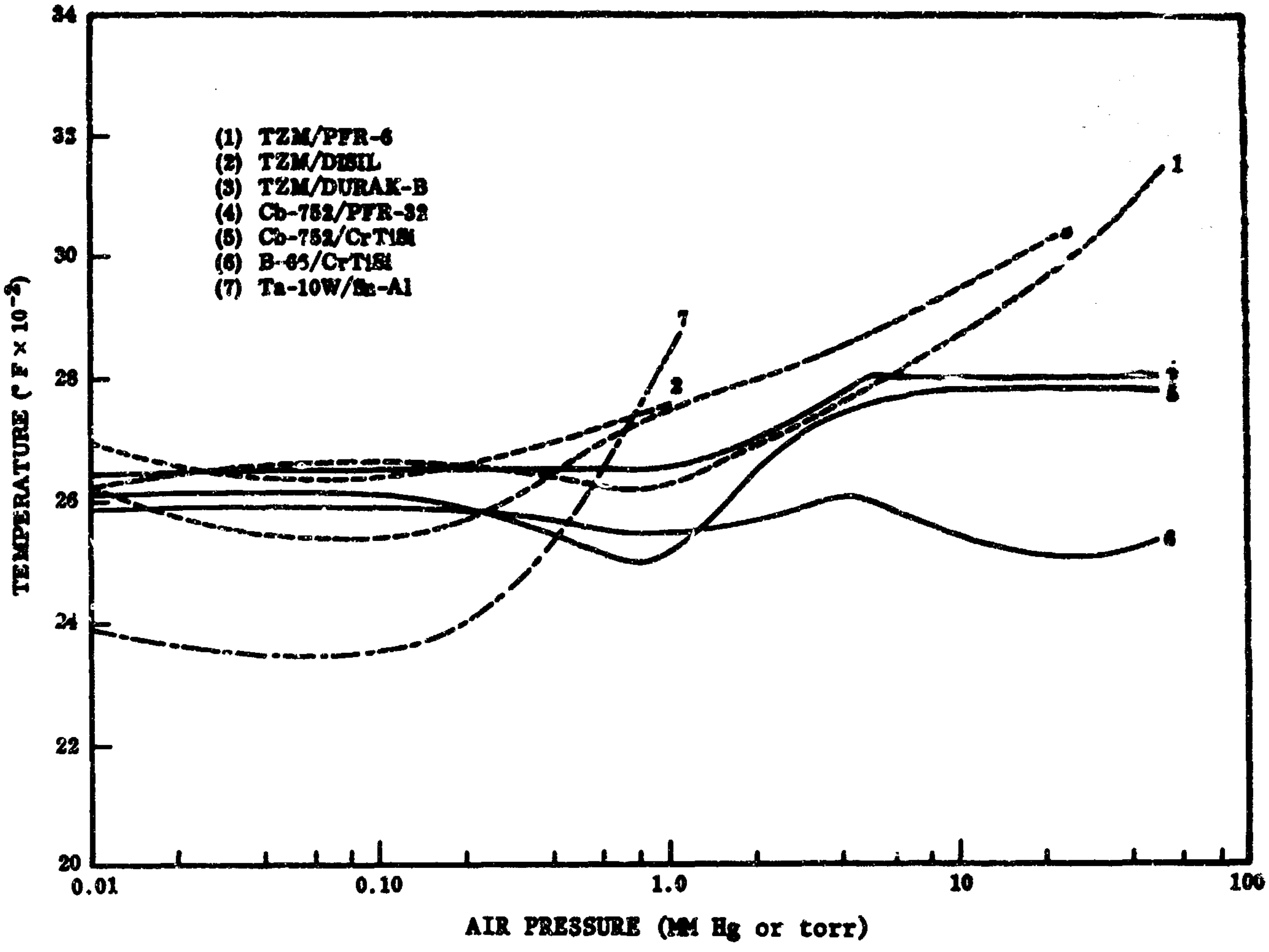

FIGURE 1. COMPARISON OF 4-HOUR RANDOM FAILURE LIMITS, BASELINE RESULTS, DETERMINED BY LOCKHEED[1]

Ta-10W poses the greatest problem with respect to vacuum exposure. In a vacuum of 10^{-5} torr, tin boils at 1600 F; at 10^{-7} torr, it boils at 1325 F.

Temperature-Pressure Cycling. This experiment, designed to simulate the conditions characteristic of lifting re-entry heat-shield panels, did not seriously degrade the protective properties of the majority of the coatings.

Acoustic Vibration Effects. None of the coating systems were damaged by exposure to sinusoidal or random vibration at high intensity levels.

Defect Tolerance. Most coating systems could be bent 10 to 30 degrees at room temperature and still retain their high-temperatures protectiveness. The Sn-Al coating had the highest resistance to defect formation.

Compatibility Problems. All coating systems presented compatibility problems with refractory oxides or other coating systems when liquid or semiliquid material was present. All silicide coatings reacted with Al_2O_3, ZrO_2, BeO, and SiO_2 at temperatures above 2600 F.

Kinetic Model Tests. The data obtained in the investigation were used successfully to make reasonable forecasts of performance capabilities and relability under varying conditions of exposure.

COATINGS FOR TANTALUM ALLOYS

Solar[2] and Vitro[3] are developing protective coatings for the T-222 tantalum alloy under the sponsorship of NASA. These coatings are intended for use in protecting gas-turbine engine nozzle vanes for a minimum of 600 hours at temperatures up to 2400 F. Solar is examining high-pressure and vacuum pack-cementation techniques for applying modified silicide coatings to T-222 alloy. Modifiers being investigated include combinations of titanium, tungsten, molybdenum, and vanadium. Electrophoretic-deposited coatings are being applied at Vitro. In preliminary tests at Vitro, WSi_2- and $MoSi_2$-base coatings have protected T-222 alloy for periods up to 600 hours at 1500 and 2400 F.

Investigations of protective coatings for tantalum alloys for use at temperatures higher than 3500 F are continuing at IITRI[4] and Solar.[5] Recent studies at IITRI have been concerned with the application of Hf-20 to 25Ta alloys by cladding and slurry processes. Dense, 6 to 12-mil-thick slurry coatings were applied using a suspension of hafnium-tantalum-copper-aluminum elemental powders and sintering at about 2300 F in vacuum. Total copper-plus-aluminum content in these coatings is about 4 weight percent. Coating lives in excess of 15 minutes have been obtained at 3500 F in oxygen-hydrogen-torch tests. Unalloyed iridium coatings and iridium-rhodium coatings are being electrodeposited onto tungsten in the studies being conducted at Solar. Tungsten is a potential diffusion barrier (to prevent liquation) between the tantalum substrate and the iridium coating. Tests of a 3-mil-thick unalloyed iridium coating on tungsten wire showed that the coating provided protection for 47 minutes in air at a corrected temperature of 4200 F.

PLATINUM COATINGS

Metals and Controls has concluded an evaluation of the use of platinum as a protective coating for columbium and molybdenum alloys.(6) The majority of this effort was directed toward the examination of potential diffusion barriers to stop the transfer of degrading substrate elements into the platinum coating. Barriers that were examined included: tungsten, W-25 at.% Re-30 at.% Mo alloy, rhenium, hafnium, iridium clad to tungsten, silicon carbide, zirconia, alumina, and magnesia. Test specimens consisting of these various barriers, 1/2 to 3 mils thick, sandwiched between columbium alloy FS-85 or molybdenum TZM and 3-mil-thick platinum were oxidation tested at 2550 F in air flowing at 240 ipm. The performance of these specimens was compared to that of specimens having 3-mil and 5-mil platinum coatings with no diffusion barriers. Many of the barrier-containing specimens had coating lives greater than 16 hours at 2550 F, which is characteristic of the 3-mil platinum-coated specimens without diffusion barriers. However, none of the barrier-containing systems exceeded the life of the 5-mil platinum-coated specimens of 50 to 66 hours.

The appendix of the Metals and Controls report contains a detailed analysis of the diffusion behavior of Pt/FS-85 and Pt/TZM couples and the difference in platinum-coating-failure mechanisms for solid oxide (columbium) and gaseous oxide (molybdenum) forming substrates.

OXIDATION OF COMPLEX SILICIDES

The oxidation behavior of complex silicide compositions in high-temperature atmospheric and low-pressure tests were described by Boeing personnel at an American Ceramic Society meeting.(7) The objective of this study was to identify oxidation-resistant compositions suitable for use as coating materials in re-entry applications.

Intermetallic compounds based on $MoSi_2$, WSi_2, $CbSi_2$, and $TaSi_2$ were prepared by a sintering-plus-arc melting operation. The various compositions were tested at (1) 2900 F in ambient air and (2) 2800 F in reduced air pressure (0.1 to 0.5 torr). Modifiers which were investigation included: aluminum, boron, cerium, chromium, hafnium, nickel, thorium, titanium, vanadium, yttrium, and zirconium.

Nearly all the $MoSi_2$- and WSi_2-base specimens tested in the 2900 F atmospheric test performed satisfactorily, most gaining less than 10 mg/cm² in 40 hours. However, very few compositions were found that possessed good low-pressure oxidation resistance. Compositions that did show substantial improvement at low pressures were $MoSi_2 \cdot 10TaB_2$ and $MoSi_2 \cdot 10TiB_2$.

While the general performance of the $MoSi_2$ and WSi_2 systems was good at atmospheric pressure, the opposite was generally true for the $CbSi_2$- and $TaSi_2$-base systems. Most of the modified $CbSi_2$ and $TaSi_2$ compositions did show an improvement over the base systems, however. Silicides of tantalum and columbium demonstrating much improved behavior in both the high-pressure and low-pressure tests had the compositions $(Cb_{0.9}Ti_{0.1})\,Si_2$, $(Cb_{0.75}V_{0.25})\,Si_2$, $(Cb_{0.9}Ti_{0.1})\,(Si_{0.8}Al_{0.1}B_{0.1})_2$, and $(Ta_{0.9}Ti_{0.1})\,(Si_{0.8}Al_{0.1}B_{0.1})_2$. The beneficial effects of vanadium as a modifier for silicide coatings on columbium alloys has been further documented in the fluidized-bed coating studies now in progress at Boeing.

REFERENCES

(1) Perkins, R. A., and Packer, C. M., "Coatings for Refractory Metals in Aerosapce Environments", Report AFML-TR-65-351, Lockheed Missile and Space Company, Palo Alto, Calif., Contract AF 33(657)-11150 (September, 1965) DMIC No. 64151.

(2) Stansfield, O. M., Wimber, R. T., and Stetson, A. R., "Development of Coatings for Tantalum Alloy Nozzle Vanes", Report RDR 1396-1, Solar Division of International Harvester Company, San Diego, Calif., Contract NAS3-7276 (October 29, 1965) DMIC No. 63986.

(3) Ortner, M. H., and Klach, S. J., "Development of Protective Coatings for Tantalum T-222 Alloy", Report VL-2403-7-0, Vitro Laboratories, West Orange, N. J., Contract NAS 3-7613 (December 20, 1965) DMIC No. 63653.

(4) Preliminary information reported by IIT Research Institute, Chicago, Ill., under an Air Force contract.

(5) Preliminary information reported by Solar Division of International Harvester Company, San Diego, Calif., under an Air Force contract.

(6) Girard, E. H., Clarke, J. F., and Briet, H., "Study of Ductile Coatings for the Oxidation Protection of Columbium and Molybdenum Alloys", Final Report, Metals and Controls, Inc., Division of Texas Instruments, Inc., Attleboro, Mass., Contract NOw 65-0340-f (May, 1966) DMIC No. 64575.

(7) Regan, R. E., Baginski, W. A., and Krier, C. A., "Oxidation Studies of Complex Silicides for Protective Coatings", Boeing Company, Seattle, Wash., paper presented at the Spring Meeting of the American Ceramic Society, May 9, 1966, DMIC No. 64611.
